MEMOIRS

OF THE

COLLEGE OF SCIENCE

KYOTO IMPERIAL UNIVERSITY

VOL. VI, NO. 4

MARCH 1923

KYOTO

ERRATA to Vol. VI, No. 4.

Page 177, line 3 from bottom in foot-note, for (1800), read (1890).

Picrates of Some Tertiary Amines. Reply to Professor B. K. Singh.

By

Shigeru Komatsu and Umesaburo Takimoto.

(Received September 5, 1922)

Some years ago one of us proposed the picrate-method[1] for the identification of tertiary amines by determing the meltining point of the picrates. K. B. Singh,[2] however, applying the method for identification of the amines formed by the decomposition of hydrazonium compounds, claimed that the tertiary amines used for the experiment by one of us were impure, since the picrates of the amines showed low melting points compared with his substances.

Now, in order to determine whether Prof. Singh's announcement is really true, the authors have undertaken the present study.

The aniline used for starting material was pure Kahlbaum's sample was purified by fractional distillation three times under ordinary pressure. 70 grm. of pure methyl aniline and 68 grm. of pure ethyl aniline were prepared from 250 grm. pure acetanilide (M. p. 112°) 65 grm. metallic sodium and 420 grm. pure methyl iodide (B. p. 43°) and from 250 grm. pure acetanilide and 430 grm. pure ethyl iodide (B. p. 72–3°) respectively, by following Hepp's direction,[3] and were separated from the aniline by means of carbon bisulphide.[4]

The secondary amines thus obtained were purified by fractional distillation three times under ordinary pressure and then once under

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1 Mem. Coll. Sci. Engin. Kyoto, **3**,371 (1912).

2 J. Chem. Soc., **109**,789 (1916).

3 Ber. D. Chem. Ges., **10**,327 (1877).

4 Ibid., **8**,105 (1875).

reduced pressure. They were colourless oils and showed the following physical constants:

Table I.

	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$	B. p.	M. R.
Methyl aniline	0.97945	1.5630	190.5–191° (760.6 mm.) 85–85.5° (12 mm.)	35.53
Ethyl aniline	0.95645	1.5487	200.5–201° (755 mm.) 97° (18 mm.)	40.27

20 grm. pure diethyl aniline and 8 grm. pure methyl ethyl aniline were prepared from an equimolecular mixture of 32 grm. pure ethyl aniline and ethyl and methyl iodides respectively, particular care being taken to avoid the replacement of ethyl group in the amine molecule by methyl group during methylation of the secondary amine.[1] The tertiary amine was separated from the secondary amine by the aid of benzensulphonyl chloride,[2] and then fractionated on metallic sodium three times under ordinary pressure and once under reduced pressure. In the same way, 12 grm. pure dimethyl aniline and methyl ethyl aniline were obtained from 34 grm. methyl aniline and methyl iodide and ethyl iodide respectively, and were purified.

The tertiary amines thus obtained were colourless liquids, and the density and index of refraction of the base were determined, with the results shown in the following table:

Table II.

	$d_{4^\circ}^{25^\circ}$	$n_D^{25^\circ}$	B. p.	M. R.
Dimethyl aniline	0.9545	1.5551	188.5–9.5° (752.5 mm.) 86.5–87° (19 mm.)	40.34
Diethyl aniline	0.93061	1.5376	209.5–9.8° (748 mm.) 108.5° (18 mm.)	50.11
Methyl ethyl aniline				
from methylaniline	0.94028	1.5446	97.5–98° (19 mm.) 200.5–1.5° (753 mm.)	45.42
„ ethyl aniline	0.94026	1.5444	200.5–1.5° (753 mm.) 99–99.5° (25 mm.)	45.42
„ Merck	0.94426	1.5451	200.5–1.5° (758 mm.) 119.5–20° (38 mm.)	45.16

[1] H. O. Jones: J. Chem. Soc., **87**,1721 (1905); H.O. Jones and J. R. Hill: Ibid., **91**,2083 (1907).

[2] O. Hinsberg: Ber. D. Chem. Ges., **23**,2963 (1890); O. Hinsberg and J. Kepler: Ibid., **38**,906 (1905).

The melting point of the picrates formed from equimolecular mixture of the tertiary amine and picric acid in an alcoholic solution, was determined, and the results are shown in the following table with that observed in the case of the picrate of methyl ethyl aniline from Merck, which was formerly used by one of us in the experiments with quaternary ammonium compounds, and was purified by fractional distillation under ordinary pressure and then under 19 mm. pressure.

Seeing that the methyl ethyl aniline prepared from methyl aniline and ethyl iodide was somewhat impure as indicated by the melting point of the picrate (*a*), the amine was again treated with benzensulphonyl chloride to remove some secondary amine admixed, and then the tertiary amine was purified as usual. The physical constant of the base (Table II) and the melting point (*b*) of the picrate quite agree with those of methyl ethyl aniline from ethyl aniline and methyl iodide.

Table III.

Melting Point of Picrates.

	Dimethyl aniline	Diethyl aniline	Methyl ethyl aniline from methyl aniline (*a*)	Methyl ethyl aniline from methyl aniline (*b*)	Methyl ethyl aniline from ethyl aniline	Merck.
A	158–159.5°	137.5–139°	125.5–126°	126–127°	127.5–128°	125–127°
A_1	157–158°	137.5–139°	125–126°	124.5–126°	127–128.3°	122–127°
A_2	116–116.5°	122–135°	127–128°	123.5–124°	126.5–127°	94–118°
B	158–159.5°	137.5–139°	126–127°	126.5–127°	127.5–128.1°	128–129.5°
B_1	157–159.5°	137.5–139°	123–124.5°	126–127.5°	127.8–128.2°	124.5–126.5°
C	—	137–138.5°	129–131°	126–127°	127.8–128.3°	128.5–130°
C_1	—	137–139°	126–127°	126–127°	127.5–128.3°	128.5–130°
E	—	—	132–137.5°	125.5–127.3°	127.5–128°	127.5–128.5°
E_1	—	—	—	125–126.5°	127–128.3°	128–129°

A_1 Crystals obtained on concentrating the filtrate from A in vacuo.

A_2 Crystals obtained on concentrating the filtrate from A_1 on water bath.

B Crystals obtained from A from alcohol solution.

B_1 Crystals deposited on concentrating the filtrate from B on water bath.

C Crystal,—B recrystallized from alcoholic solution.

C_1 Crystal deposited on concentrating the filtrate from C on water bath.

E Crystal,—C recrystallized from alcoholic solution.

E_1 Crystal deposited on concentrating the filtrate from E on water bath.

Table IV.

M. p. of Picrates			
Amines	Komatsu[1]	Singh[2]	Authors
$C_6H_5N(CH_3)_2$	154–155°	163–164°	158–159.5°
$C_6H_5N(C_2H_5)_2$	135–136°	142°	137–138°
$C_6H_5N.CH_3C_2H_5$	124–125°	134–135°	127–128.3°

June, 1922, Laboratory of Organic and Bio-Chemistry.

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1 Loc. cit.

2 Loc. cit.

Studies on Catalytic Action, I. Catalytic Reduction of α-Naphthol and α-Naphthylamine.

By

Shigeru Komatsu and Ryuzaburo Nodzu.

(Received September 5, 1922)

Ar-Tetrahydro-α-naphthol and ar-tetrahydro-α-naphthylamine were prepared by Bamberger and his collaborators[1] by the action of sodium and boiling amylalcohol on α-naphthol and α-naphthylamine respectively. H. Lerowx,[2] however, has reported that decahydro-α-naphthol and decahydro-α-naphthylamine were formed when α-naphthol and α-naphthylamine were reduced with hydrogen and reduced nickel at 200°. On the other hand, Professor P. Sabatier[3] succeeded in preparing tetrahydronaphthalene by reducing naphthalene with hydrogen in the presence of nickel.

Authors, therefore, expected that ar-tetrahydro-α-naphthol would be obtained from α-naphthol by catalytic reduction, when the favorable conditions had been discovered for effecting the partial reduction of the compound.

15 grm. pure α-naphthol (m. p. 95–96°) prepared by the potash-fusion of α-naphthalenesulphonic acid and then purified by steam distillation, were passed with pure hydrogen over reduced nickel heated to 100–110°, and 11.7 grm. of the reaction product were obtained. The product, proved free from naphthol by the conc. sulphuric acid-nitrous acid test, was extracted with 10% caustic potash solution. The caustic alkaline solution after washing with ether to remove

1 Ber. D. Chem. Ges., **23**, 215 (1800); **21**, 1786 (1886).
2 C. R., **141**, 953 (1905); Ann. chim. phys., (8) **21**, 483 (1910).
3 C. R., **132**, 1254 (1901).

neutral substances completely, was acidified with diluted hydrochloric acid, whereupon 4.9 grm. of crude hydrogenated naphthol separated which was then purified by distillation under 750 mm. and collected fraction boiling at 262–266°. The yield was 2 grm.

It was soluble in dilute caustic alkaline solution and organic solvents but scarcely in ammonia water. It melted at 68.5°, and yielded azo-compound with diazobenzene chloride. The physical and chemical properties so far studied agree with those of ar-tetrahydro-α-naphthol prepared first by Bamberger.[1] For confirmation, the substance was oxidized with potassium permanganate, and oxalic and adipic acids were isolated from the oxidation product. The latter compound was identified by its melting point (m. p. 148.5–149°) and the preparation of a characteristic copper salt of the acid. On analysis of the hydrated naphthol, it gave the following results:

0.1370 grm. substance gave 0.4043 grm, CO_2 and 0.1019 grm. H_2O.

	Calc. for $C_{10}H_{12}O$.	Found.
C	81.03	80.49
H	8.17	8.32
O	10.80	—

The oily substance, insoluble in caustic potash solution, was extracted with ether; the ether being distilled off from the solution, the residual oil amounted to 6 grm. It was subjected to fractional distillation under 22 mm., and 3.5 grm. A fraction, B. p. 100–130°, and 1.5 grm. B fraction, B. p. 130–155°, were separated. The B fraction was confirmed to consist of α-ketotetrahydronaphthalene by converting into its semicarbazone in the manner described by F. S. Kipping and Hill.[2] The melting point and solubility of the semicarbazone agree with those of Kipping's compound. On analysis of the semicarbazone, it gave the following results:

0.1005 grm. substance gave 0.2356 grm. CO_2 and 0.0611 grm. H_2O.

	Calc. for $C_{11}H_{13}ON_3$.	Found.
C	65.00	63.91
H	6.48	6.80

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[1] Loc. cit.; P. Jacobson and A. Turnbull: Ber. D. chem. Ges., **31**, 897 (1898).

[2] J. Chem. Soc., **75**, 144 (1899).

A fraction was also studied and was found to consist of tetrahydronaphthalene by the analysis and determination of density and index of refraction of the purified substance (B. p. 202–4°, 753 mm.), distilled under ordinary pressure and then on metallic sodium.

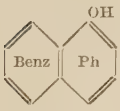
0.1258 grm. sub. gave 0.4161 grm. CO_2 and 0.1102 grm. H_2O.

	Calc. for $C_{10}H_{12}$.	Found.
C	90.84	90.22
H	9.16	9.80
	$n_D^{25°} = 1.5327$	$d_{4°}^{25°} = 0.9629$

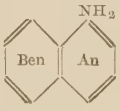
In another experiment, 11 grm. of the product were obtained from 15 grm. α-naphthol by reducing at 135–145°, from which 1 grm. pure ar-tetrahydro-α-naphthol, and 10 grm. of a mixture of keto-tetrahydronaphthalene and tetrahydronaphthalene, were isolated.

The formation of both tetrahydronaphthalene and α-keto-tetrahydronaphthalene from α-naphthol was easily explained by assuming the intermediate formation of ac-tetrahydro-α-naphthol, since naphthol could be presumed to behave analogously as phenol did toward the reducing agent. We were, therefore, led to the conclusion that α-naphthol upon reduction with hydrogen in the presence of reduced nickel at 100–110° simultaneously 41% crude ar-tetradydro-α-naphthol (20% pure comp.) and 51% ac-tetrahydro-α-naphthol, but at 135–145°, 10% pure ar-compound and 90% ac-compound.

α-Naphthol may be regarded as a phenol derivative in consideration of the substitution of the benzene nucleus by the hydroxyl group and on the other hand as a benzyl alcohol derivative, in respect of the non-substituted nucleus:



Benz = Benzyl alcohol
Ph = Phenol



Ben = Benzyl amine
An = Aniline

The difference in the yield of the reducing substances from α-naphthol as above mentioned can be viewed as that which prevails between benzylalcohol and phenol derivatives towards the reducing agent.[1] In the same way, when α-naphthylamine is regarded as a condensed com-

1 P. Sabatier and Senderens: C.R., 137, 1025 (1903).

pound of benzylamine and aniline, a fruitful result in the yield of ar-tetrahydro-α-naphthylamine from α-naphthylamine by catalytic reduction can easily be anticipated by referring to the results of aniline and benzylamine.[1] 20 grm. α-naphthylamine (B. p. 174–6°, 20 mm.) obtained from a commercial substance by fractional distillation at reduced pressure, was reduced with hydrogen in the presence of reduced nickel at 135–145°, and 16 grm. of the product were obtained. The product was treated with dilute hydrochloric acid and the acid solution separated from the insoluble oil was alkalined with caustic potash solution after washing with ether to expel a hydrocarbon formed simultaneously during the catalytic reduction. The basic substance thus isolated after drying with anhydrous sodium sulphate was fractionated 3 times at ordinary pressure.

20 grm. α-naphthylamine :

16 grm. reaction product.

1.2 grm. crude hydrocarbon.

10 grm. crude hydrogenated base, B. p. 260–278° 752 mm.

4 grm. crude α-naphthylamine, B. p. above 278°, 752 mm.

The crude hydrogented base was purified by distillation at ordinary pressure and also under reduced pressure, of the fraction boiling at 156–160°, 22 mm., the density and the index of refraction were determined : $d_{4^\circ}^{25^\circ} = 1.0500$ and $n_D^{25^\circ} = 1.5829$.

It yielded a diazonium chloride and azo-compound. As far as could be judged, the main portion of the fraction, B. p. 260–278°, consisted of ar-tetrahydro-α-naphthylamine which was formerly obtained by Bamberger[2] by a different method. In order to confirm the idea, the substance was analysed :

0.1350 grm. sub. gave 0.4052 grm. CO_2 and 0.1094 grm. H_2O.

0.1390 grm. sub. gave 0.01285 grm. N by Kjeldahl's method.

	Calc. for $C_{10}H_{13}N$	Found.
C	81.57	81.86
H	8.90	9.06
N	9.52	9.25

[1] P. Sabatier and Senderens : C. R., **138**, 457 (1904); P. Sabatier and Mailhe : Ibid., **153**, 160 (1911); P. Sabatier : La Catalyse en Chimie Organique. 1920, p. 177.

[2] Loc. cit.

On the other hand the base was converted into naphthol with nitrous acid and the resulting ar-tetrahydro-α-naphthol[1] was confirmed by its elementary analysis:

0.068 grm. sub. gave 0.2015 grm. CO_2 and 0.0523 grm. H_2O.

	Calc. for $C_{10}H_{12}O$	Found.
C	81,03	80.82
H	8.17	8.60

A mixture of the hydrogenated naphthol thus obtained and that from α-naphthol by direct reduction showed no lowering in the melting point (m. p. 68.5°).

The hydrocarbon separated from the basic portion of the reaction product was found to boil at 204–6°, and was confirmed to be tetrahydronaphthalene[2] by its analysis:

0.0958 grm. sub. gave 0.0760 grm. H_2O and 0.3190 grm. CO_2.

	Calc. for $C_{10}H_{12}$.	Found.
C	90.84	90.81
H	9.16	8.88

Of the reaction product from α-naphthylamine by catalytic reduction at 135–145°, obtained 90% ar-tetrahydro-α-naphthylamine and 10% ac-tetrahydro-α-naphthylamine and the latter transformed into tetrahydronaphthalene and thus our hypothesis was proved.

Reduction temp.		Percentage of reduction product	
		ar-tetrahydro-comp.	ac-tetrahydro-comp.
Naphthol	100–110°	20 (41 as crude sub.)	(51 as crude sub.)
	135–145°	10	90
Naphthylamine	135–145°	90	10

(July, 1922. Laboratory of Organic & Bio-chemistry.)

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1 A. G. Green & F. M. Rowe: J. Chem. Soc., **113**, 965 (1918); E. Bamberger & M. Althause: Ber. D. Chem. Ges., **21**, 1893 (1888).

2 C. Graebe and P. A. Guye: Ber. D. chem. Ges., **16**, 3028 (1883).

Studies on Catalytic Action, II. Catalytic Preparation of para-Cymene and Its Formation in Sulphite Terpentine.

By

Shigeru Komatsu, Hisashi Nakamura and Masao Kurata.

(Received November 16, 1922)

Klason[1] first noticed that the etherial oil collected during the manufacture of pulp from spruce by the sulphite process, consists mainly of para-cymene and not of terpenes. Sulphite terpentine from the pulp mills of U. S. A. was studied by Herty and Graham,[2] A.W. Schorger[3] and M. Philips[4] with a view to the utilization of para-cymene in it. O. Aschan[5] and J. Alfthan[6] have, also, studied the terpentine in Finland.

The sulphite terpentine, we studied, was obtained from the pulp mill at Ochiai, Karafuto, where sulphite pulp was manufactured from Yezo-matsu and Todo-matsu. The crude oil which amounted to 140 grm., was dark brown in colour, $d_{4^\circ}^{15^\circ}=0.965$. It was subjected to steam distillation and a light-yellow oil was obtained, which, after drying with anhydrous sodium sulphate, was distilled:

First fraction, B. p., 174–270°.	70 grm.
Second fraction, B. p., above 270°.	35 grm.

Two fractions were fractionated on metallic sodium, and the fraction boiling at 173–175° was collected. The yield was 50% of the crude oil.

1 Ber. D. Chem. Ges., **33**, 2343 (1900).
2 J. Ind. & Eng. Chem., **6**, 803 (1914).
3 Ibid., **10**, 258 (1918).
4 J. Amer. Chem. Soc., **44**, 1775 (1922).
5 Zellstoff Chem. Abhand., 1,73 (1920).
6 Ber. D. Chem. Ges., **53**, 78 (1920).

The physical constants and the elementary composition of the purified substance were determined with the following results:

It gave C=89.33; H=10.34; ($C_{10}H_{14}$, requires C=89.48; H=10.52), $d_{4^\circ}^{25^\circ}=0.85381$; $n_D^{25^\circ}=1.4821$; M.R.=44.80.

For identification with para-cymene, it was oxydized with potassium permanganate into tere-phthalic acid[1] and para-hydroxyisopropyl benzoic acid[2] and the latter melts at 156° and gave on analysis C=66.23; H=6.64; ($C_{10}H_{12}O_3$ requires C=66.64; H=6.72).

On the other hand, the substance was sulphonated with conc. sulphuric acid following Claus' directions,[3] and sodium salts of mono- and di-sulphonic acids were separated by aid of their solubility in alcohol solution, and di-sulphonic acid salt was analysed; Ba=31.32($C_{10}H_{12}O_6S_2Ba$ requires Ba=31.95).

Terpenes of the formula $C_{10}H_{16}$ by dehydrogenation, were ultimately converted into para-cymene; consequently the transformation was sometimes made use of in the determination of the constitution of the compounds.[4]

Kekule[5] has studied the conversion of terpene into cymene by oxydation with phosphorous sulphide. L. Ruzika, J. Meyer and M. Mingazzini[6] have obtained para-cymene from limonene and terpinene by catalytic oxydation with sulphur, following Vesterberg's directions,[7] and the same process was applied by W. Friedmann[8] to naphthene hydrocarbons.

The authors have succeeded in the catalytic preparation of para-cymene, the main constituent of sulphite terpentine, from pinene and menthene respectively.

136 grm. pinene obtained from commercial terpentine oil, were heated with 70 grm. sulphur in a flask at 200° for 23 hours, the reaction product was distilled under reduced pressure and 71.5 grm. of the product was obtained. It was distilled under ordinary pressure

1 R. Fittig, A. Kobrich & T. Jilke: Lieb. Ann., **145**, 144 (1868).
2 O. Wallach: Ibid., **264**, 10 (1891).
3 Ber. D. Chem. Ges., **14**, 2140 (1881).
4 V. Meyer & P. Jacobson: Lehrbuch d. Org. Chem., II. 110 (1902).
5 Ber. D. Chem. Ges., **2**, 121 (1869).
6 Hel. Chim. Acta, **5**, 356 (1922).
7 Ber. D. Chem. Ges., **36**, 4200 (1903).
8 J. Chem. Soc., **112**, 13 (1917).

after treating with 10% caustic soda solution, dried with calcium chloride, and a fraction boiling at 170–275° was collected. The yield was 55 grm. (52% of the theoretical).

The product, thus obtained, on distilling with metallic sodium, was all distilled out between 165–175°. It was purified by repeated distillation with metallic sodium.

The purified substance $d_{4°}^{25°} = 0.8542$; $n_D^{25°} = 1.4743$; M.R.=44.41, was analysed; it gave C=88.37; H=11.34; ($C_{10}H_{14}$ requires C=89.45; H=10.55.).

It was oxydised with potassium permanganate into para-hydroxy-isopropyl benzoic acid[1] which melted at 156–156.5° and gave C=66.44; H=6.33; ($C_6H_4C(OH)(CH_3)_2COOH$ requires C=66.64; H=6.72).

In the same manner, menthene prepared from menthol by catalytic dehydration with thoria was transformed into para-cymene.

140 grm. menthol were passed on thoria heated at about 400°, and yield 125 grm. light greenish yellow liquid substance, $d_{4°}^{25°} = 0.817$, which distilled between 155–210°. It was purified by repeated distillation with metallic sodium, and the following fractions were obtained:

The fraction boils at 145–164° under 752 mm., with 10% of the yield.

Other fraction boils at 164–167° under 752 mm., with 40% of the yield.

The second fraction was confirmed by analysis to consist of menthene,[2] $d_{4°}^{25°} = 0.8096$; $n_D^{25°} = 1.4469$; M.R.=45.60; which gave C=86.10; H=12.92; ($C_{10}H_{18}$ requires C=86.87; H=13.13).

Menthene, thus obtained, was heated with sulphur at 200° for 24 hours, and the reaction product was subjected to distillation on metallic sodium to purify. The cymene fraction boiling at 170–173.5°, $d_{4°}^{25°} = 0.8389$, $n_D^{25°} = 1.4740$; M.R.=44.94; gave on analysis C=87.68; H=10.92, ($C_{10}H_{14}$ requires C=89.45; H=10.55).

The conversion of menthol and borneol by simply heating with sulphur at about 200° into cymene, was tried but with no result.

Terpenes of the formula $C_{10}H_{16}$, on the contrary, can easily be transformed into cymene by catalytic oxydation with sulphur.

Aromatic hydrocarbons and their oxygen derivatives such as para-cymene and safrol are widely distributed, being generally associated

1 O. Wallach: Loc. cit.

2 P. Walter: C. R., **6**, 473 (1838); Lieb. Ann., **32**, 288 (1839).

with the essential oils in plants. The origin and the mechanism of the formation of the aromatic compounds in the flora were interesting problems.

As to the formation of para-cymene in sulphite terpentine, Klason[1] has already put forward the following opinion :

„ Alles Terpentinöl soll ja auch nach den vorhandenen Angaben etwas Cymol enthalten, und im Holze sind die aetherische Oele lange Zeit dem Einfluss der Luft ausgesetzt worden. Wie man nun diesen Uebergang im Lichte der Engler'schen Theorie der Autoxydation erklären soll, mögen künftige Untersuchungen darthun. Entweder wurden von der zunächst entstandenen superoxydartigen Verbindung zwei Wasserstoffatome direct wegoxydirt oder es entsteht intermediär ein Alcohol, welcher durch Wasserabspaltung in Cymol übergeführt wird." Much more probably the formation of cymene in wood may be attributed to the autoxydation of etherial oils, as Klason stated. Whether the sulphite terpentine was formed in a digester during the manufacture of pulp, by the same mechanism is very doubtful.

Our hypothesis, however, for the formation of the sulphite terpentine, is quite different from Klason's, and is grounded on the experiments described above; the terpene existing in the wood would probably be transformed during the manufacture of pulp by the sulphite process, into para-cymene by catalytic oxydation with sulphur which is liberated in a free state in the digester.

The evidences in favor of our view of the formation of sulphite terpentine, are easy to quote here from literature.

Shinozaki[2] has isolated from the essential oils obtained by steam distillation of Yezo-matsu and Todo-matsu pinene and phellandrene, which were proved by our experiments to transform into para-cymene.

We cannot pass over without mention here the most important fact that free sulphur actually exists in the acid-liquor used for pulp manufacture, cited in Klason's article.[3]

October 1922, Organic-Biochemical Laboratory.

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1 Loc. cit.

2 Kogyo-Kwagaku Zasshi, **15**, 730 (1912).

3 Üregelmassige Gang v. Sulphitstoff-Kochung u. desen Ursache, 1910, p. 63.

Vol. VI, No. 4, Published March 20th, 1923.

Price - - - Yen .40

These Memoirs are on sale at

MARUZEN COMPANY, LTD.

TOKYO, OSAKA, KYOTO, NAGOYA, YOKOHAMA, FUKUOKA & SENDAI.

大正十二年三月十七日印　刷
大正十二年三月二十日發　行

編纂兼發行者　京都帝國大學理學部

印刷者　大久保秀次郎
東京府下荏原郡世田谷字下町五十番地

印刷所　株式會社　東京築地活版製造所
東京市京橋區築地二丁目十七番地

賣捌所　丸善株式會社
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